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Exceptionally Fast Carbon-Carbon Bond Reductive Elimination from Gold(III)

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Abstract

Reductive elimination of carbon-carbon (C-C) bonds occurs in numerous metal-catalyzed reactions. This process is well documented for a variety of transition metal complexes. However, C-C bond reductive elimination from a limited number of Au(III) complexes has been shown to be a slow and prohibitive process, generally requiring elevated temperature. Herein, we show that oxidation of a series of mono- and bimetallic Au(I) aryl complexes at low temperature generates observable Au(III) and Au(II) intermediates. We also show that aryl-aryl bond reductive elimination from these oxidized species is not only among the fastest observed for any transition metal, but is also mechanistically distinct from previously studied alkyl-alkyl and aryl-alkyl reductive eliminations from Au(III).

Reductive elimination of C-H, C-C, and C-X bonds is a key step in many metal-catalyzed reactions.[1] These processes have been extensively studied from Ni[2–6], Pd[7–15], and Pt[16–22], yet relatively little is known about the reductive elimination from Au, which is markedly more stable toward air and water. In fact, since Kochi[23–25] and Tobias's[26] seminal investigations of high-temperature dialkylgold(III) reductive eliminations over 35 years ago, fundamental studies of C-C bond reductive coupling from oxidized Au centers remain exceedingly rare. Previous studies have shown that *cis*-EtMe$_2$Au(PPh$_3$)[24] and [*cis*-(CH$_3$)$_2$Au(PPh$_3$)$_2$](PF$_6$)[26] are stable at room temperature, undergoing alkyl-alkyl bond reductive elimination at 70 °C (k_{obs} ~ $10^{-5} - 10^{-3}$ s^{-1}), while *cis*-(CH$_3$)$_2$AuCl(PPh$_3$)[25] reductively eliminates ethane slowly at 40 °C (k_{obs} ~ 10^{-7} s^{-1}). These processes are inverse first-order in PPh$_3$ and are severely inhibited by even small amounts of free ligand. Kinetic analysis suggests that reductive elimination does not occur directly from the 4-coordinate complex, but rather from a high-energy T-shaped intermediate, formed by slow, reversible phosphine dissociation[23]. Since these reports, the field has not only witnessed the advent and maturation of now-ubiquitous palladium-catalyzed cross-coupling methods, but the development of homogeneous redox-neutral gold catalysis as well. The shortage of mechanistic insight of processes at Au(III) may be due in part to synthetic challenges in

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Author Contributions

M. S. W. and W. J. W. conceived, designed and performed the experiments, analyzed the data and wrote the manuscript; M. S. W. derived kinetic models; W. J. W. performed crystallographic analysis.

accessing appropriate Au(III) models, and to the high oxidation potential of Au(I) that traditionally precludes Au(I)/Au(III) redox cycling[27].

Electronic cooperation between metal centers is well established in redox processes. Hence, bimetallic Au complexes may be useful systems for studying the fundamental chemistry of oxidized organogold species. In the bimetallic core, each Au(I) can formally undergo a one electron oxidation, resulting in two d^9 metal centers with unpaired electrons capable of making a Au(II)-Au(II) σ-bond. Indeed, Fackler[28–34] and Laguna[35–38] have shown that dihalides and alkyl halides oxidize A-frame bimetallic Au(I) complexes to access Au(II) species, yet reductive elimination processes from Au(II) have not been rigorously investigated. In fact, well-behaved reductive eliminations of carbon-carbon bonds from bimetallic Au(II) species are incredibly rare[39]. Due to the preference for linearity by Au(I), A-frame bimetallic Au(I) complexes lack available coordination sites and may only coordinate nucleophiles upon oxidation. Therefore, while non-A-frame systems may be more appropriate for mechanistic studies that ultimately inform catalysis, only one non-A-frame bis(aryl) bimetallic Au(II) complex has been prepared[38]; due to the strongly electron-withdrawing perfluorinated aryl ligands, biaryl reductive elimination does not occur at room temperature, and reductive elimination at elevated temperatures was not investigated.

Current studies of the fundamental chemistry at oxidized gold centers are essential to establishing new modes of gold reactivity – particularly those involving redox cycling[40]. Herein we report our preparation of several monometallic and non-A-frame bimetallic bis(aryl) gold(I) complexes that allow kinetic analysis of C-C bond-forming reductive eliminations from oxidized species. Contrary to Kochi's pioneering report, we show that C-C bond reductive elimination at Au(III) is not necessarily a "disfavored"[41,42] process, but is among the fastest C-C bond-forming reductive eliminations reported for *any* transition metal complex between −50 and −10 °C. In one case, we calculate the fastest C-C bond reductive elimination recorded to date. We show that biaryl reductive elimination at monometallic Au(III) proceeds via an unexpected mechanism, and report the mechanism of biaryl reductive elimination from non-A-frame bimetallic gold complexes.

Results and discussion

Biaryl reductive elimination from a mononuclear gold complex

Ph$_3$PAu(4-F-C$_6$H$_4$)$_2$Cl (**3**) was synthesized upon partial oxidation of Ph$_3$PAu(4-F-C$_6$H$_4$) (**1**) with PhICl$_2$ at −78 °C, followed by fast transmetalation from remaining **1** to Ph$_3$PAu(4-F-C$_6$H$_4$)Cl$_2$ (**2**) (Figure 1). The reaction is unaffected by equimolar or excess amounts of oxidant, indicating that transmetalation from **1** to **2** is faster than oxidation of **1**. While **3** cannot be isolated, the *cis*-aryl relationship is supported by ^{19}F (two 1:1 singlets at −118.4, −119.5 ppm) and ^{31}P NMR (one singlet at 27.9 ppm).

In light of Kochi's findings, we expected biaryl reductive elimination from **3** to require heating via a mechanism involving phosphine dissociation. However, to our surprise, **3** was immediately consumed at room temperature (20 °C), quantitatively generating 4,4'-difluorobiphenyl and (Ph$_3$P)AuCl. At −52 °C, aryl-aryl reductive elimination from **3** could be monitored by ^{19}F NMR (k_{obs} = (1.5 ± 0.1)×10^{-4} s^{-1}) (Figure 2); at −23 °C, reductive

elimination is 100 times faster (k_{obs} = 0.015 ± 0.001 s^{-1}). The observed rate constant remains unchanged over a range of concentrations, as well as in the presence of 10 equivalents of either Bu$_4$NCl or Ph$_3$PAuCl, indicating a unimolecular process that is first-order in **3**.

That reductive elimination is substantially more facile from **3** than from alkylgold(III) complexes may not simply be attributed to faster coupling of aryl-aryl relative to alkyl-alkyl bonds[9], but also suggests fundamentally different rate-determining steps and mechanisms. Contrary to what is established for alkyl reductive elimination of Au(III), excess PPh$_3$ increases the observed rate of reductive elimination (Figure 3). In the presence of 10 equivalents of PPh$_3$ at −52 °C, the rate of reductive elimination from **3** increases by an order of magnitude (k_{obs} = (1.2 ± 0.2)×10^{-3} s^{-1}); with 40 equivalents, the observed pseudo-first order rate constant is (6.2 ± 0.5)×10^{-3} s^{-1}. No new ^{19}F and ^{31}P NMR signals can be observed under these conditions. In contrast, neither Bu$_4$NCl nor radical traps such as 9,10-dihydroanthracene affect reductive elimination of **3**; furthermore, the rate remains unchanged in the presence of excess oxidant (PhICl$_2$ acts as a phosphine scavenger), precluding the scenario in which small amounts of PPh$_3$ liberated from **3** induce reductive elimination. These observations are consistent with two operative pathways to biaryl: one independent of added PPh$_3$ and another involving phosphine coordination. In the absence of added phosphine, reductive elimination occurs directly from square-planar complex **3**. In the presence of excess PPh$_3$, **3** likely undergoes associative ligand exchange to generate cation **4**, which rapidly reductively eliminates biaryl. This process is first-order in PPh$_3$ (Figure 3, right.) Since **4** is unobservable by NMR, reductive elimination from this complex must be substantially faster than from **3**, given its bulkier steric environment and cationic charge. When 10 equivalents of PPh$_3$ *and* 40 equivalents of Bu$_4$NCl are added, the rate remains unchanged from that of the phosphine-accelerated reaction, suggesting that reductive elimination from **4** is substantially faster than the reverse ligand exchange. At −52 °C, association of PPh$_3$ (k = 0.019 ± 0.001 s^{-1} M^{-1}) and reductive elimination from **4** (k ≥0.22 s^{-1}, see Supporting Information) are remarkably facile processes. We cannot definitively discount the possibility of reductive elimination from a 5-coordinate intermediate following coordination of PPh$_3$, but this scenario is unlikely for two reasons. Presumably, alkyl Au(III) complexes should behave similarly in the presence of excess PPh$_3$, but their reductive eliminations are instead drastically slowed. Secondly, while Yamamoto has demonstrated that a *cis*-arylmethylnickel(II) complex with a chelating bis(phosphine) undergoes accelerated reductive elimination in the presence of PPh$_3$ via a 5-coordinate species[2], comparisons with complex **3** are imperfect due to the potentially labile Au-Cl bond.

To our knowledge, reductive eliminations from diarylgold(III) complexes **3** and **4** are among the fastest observed C-C bond-forming reductive couplings at any transition metal center at temperatures below −20 °C. For comparison, rate constants for reductive elimination of diarylplatinum(II)[19] and palladium(II)[12] complexes have been reported between 10^{-5} − 10^{-3} s^{-1} at 95 and 50 °C, respectively, although Pd-catalyzed Kumada-Corriu couplings can be achieved at temperatures as low as −65 °C[43]. In some cases, diarylplatinum(II) systems only reductively eliminate biaryl at temperatures above 100 °C[28]. Reductive elimination rate constants of ~0.1 s^{-1} have also been reported for Ni-catalyzed oxidative homocouplings at

−35 °C[6], although the presumed diarylnickel(II) intermediate is never observed. Indeed, for a 3rd row metal, the rates of aryl-aryl reductive elimination from Au(III) are particularly impressive[44], outcompeting even C-C bond coupling in alkynylarylpalladium(IV) complexes ($k \sim 10^{-3}$ s^{-1} at −35 °C). An Eyring analysis over a 29 °C range reveals that the reductive elimination from **3** not only has an unusually small enthalpic barrier, but a small entropic contribution to the activation energy as well ($\Delta H^{\ddagger}$ = 17.2 ± 0.2 kcal/mol; $\Delta S^{\ddagger}$ = 2.0 ± 0.8 e.u.); these kinetic parameters suggest a transition state resembling **3** in which the Au-C(sp^2) bonds are mostly conserved.

It is not immediately obvious why aryl and chloride ligands drastically change the mechanism of C-C bond reductive elimination at Au(III). Generally, the barrier to aryl-aryl reductive elimination is lower than that for alkyl-alkyl reductive elimination[8], while the weaker σ-donating ability of aryl and chloride ligands relative to alkyls may increase the barrier to phosphine dissociation. The notion that "Au(III) and Pt(II) catalysts show similar reactivity"[42] is not necessarily true when redox processes are involved: at greater than 90 °C, Pt(II) biaryl complexes undergo reductive elimination at rates comparable to those observed for Au(III) at approximately −50 °C. The reason for this discrepancy in rates may lie in pronounced relativistic effects, which result in Au(I) having a strong preference for linearity over other transition metals[42]. Since the product of reductive elimination from a square planar complex is necessarily 2-coordinate, and the transition state is partway to linearity, the activation energy of reductive elimination of Au(III) to Au(I) may be less than that for other transition metals. This is reasonable considering the early transition state to reductive elimination of **3**.

Biaryl reductive elimination from bimetallic gold complexes

The unexpected redox behavior of mononuclear Au(III) species led us to investigate analogous reactivity of bimetallic gold complexes. Others have reported that bimetallic complexes with three-atom linkers do not undergo two-electron oxidation at a single Au(I), but instead undergo formal one-electron oxidation at two Au(I) centers to generate a species stabilized by a Au(II)-Au(II) bond[28–38]. Electronic cooperation between metal centers in bimetallic complexes offers a lower barrier oxidation pathway relative to a two-electron oxidation at a single metal center[45], allowing, for example, oxidation of dicationic A-frame Au(I) complexes by oxidants typically unreactive toward monocationic Au(I), such as benzoyl peroxide[34]. Furthermore, electrochemical studies and DFT calculations suggest that aurophilic interactions reduce the oxidation potential of bimetallic Au(I) species relative to mononuclear complexes[27].

To assess the role of metal-metal bonding in the C-C bond reductive elimination of oxidized gold, we prepared a bimetallic Au(I) complex stabilized by a bis(diphenylphosphinoamine) ligand Ph$_2$P-NR-PPh$_2$ (PNP)[46,47]. X-ray diffraction analysis of PNP[Au(4-F-C$_6$H$_4$)]$_2$ (**5**, R = CH$_3$) indicates an aurophilic interaction (Au(I)-Au(I) distance = 3.0357(2) Å) that is likely conserved in solution (See Supporting Information). Laguna has shown that direct oxidation of PNP[Au(C$_6$F$_5$)]$_2$ (R = H) with Cl$_2$ generates symmetric bimetallic Au(II) complex PNP[Au(C$_6$F$_5$)Cl]$_2$, which is stable at room temperature; crystallographic analysis

establishes a Au(II)-Au(II) bond (2.576(2) Å) and a *trans* relationship between chloride ligands[38].

The analogous low-temperature oxidation of **5** with PhICl$_2$ generates symmetric bimetallic Au(II) complex **6** (^{19}F NMR and ^{31}P NMR singlets at −120.4 ppm and 83.5 ppm, respectively), which undergoes slow reductive elimination at temperatures below −30 °C (Figure 4). At −23 °C, **6** undergoes first-order decay ($k = (1.6 \pm 0.3)\times10^{-4}$ s^{-1}) with concomitant formation of 4,4'-difluorobiphenyl. Without observing a mixed-valent intermediate, we cannot kinetically distinguish between a pathway involving rearrangement and reductive elimination, and one involving bimetallic reductive elimination via a 4-centered transition state[48]. However, Laguna has reported that similar PNP-supported binuclear perfluoroarylgold(II) complexes rearrange over several hours to mixed-valent Au(I)/Au(III) species[38]. Given fast aryl transmetalation and reductive elimination of mononuclear Au(III), as well as the scarcity of reported binuclear reductive elimination, we therefore favor a mechanism involving isomerization of **6** to mixed-valent species **7**, which then undergoes fast, unobservable reductive elimination. The kinetic parameters for the rate-limiting isomerization of **6** to **7** ($\Delta H^{\ddagger} = 16.9 \pm 0.4$ kcal/mol; $\Delta S^{\ddagger} = -7.8 \pm 1.6$ e.u.) are reflective of a low-barrier process with a small entropic penalty (Figure 6). This step is first-order in **6**, and unaffected by excess Bu$_4$NCl. Complex **6** also oxidizes excess ligand, presumably via chloronium transfer; therefore, phosphine dissociation is likely not a prerequisite for either isomerization or reductive elimination, since PNP(AuCl)$_2$ is formed quantitatively when no excess ligand is added, and no decomposition of liberated ligand (PNP + **6**) is observed. These results are consistent with a mechanism involving intramolecular aryl transfer from **6** to generate **7**, which then directly reductively eliminates to PNP(AuCl)$_2$ and 4,4'-difluorobiphenyl.

We reasoned that N→P π-donation in PNP-type ligands results in a barrier to N-P bond rotation that becomes significant at low temperature[49]. A more flexible ligand, such as 1,2-bis(diphenylphosphino)methane (dppm), could presumably facilitate intramolecular aryl transfer from a bimetallic Au(II) intermediate, resulting in a lower barrier to isomerization. Oxidation of dppm[Au(4-F-C$_6$H$_4$)$_2$]$_2$ (**8**) at −78 °C by PhICl$_2$ affords symmetric bimetallic Au(II) species **9** (^{19}F NMR and ^{31}P NMR singlets at −120.3 ppm and −18.2 ppm, respectively), which is consumed faster than analogous PNP complex **6** (Figure 4). Indeed, at −52 °C, **9** undergoes first-order decay, with fast appearance and slow consumption of mixed-valent Au(I)/Au(III) complex **10**, and appearance of 4,4'-difluorobiphenyl at approximately the same rate as the disappearance of **9** (Figure 5). Kinetic modeling precludes any scenario in which a bimetallic reductive elimination occurs directly from **9**. Instead, **9** likely undergoes irreversible isomerization to **10** ($k = (4.6 \pm 0.1)\times10^{-4}$ s^{-1}), which then reductively eliminates 4,4'-difluorobiphenyl at a comparable rate ($k = 3.9\times10^{-4}$ s^{-1}). At −30 °C, both reactions are immeasurably fast. While PNP-supported Au(I)/Au(III) species **7** could not be observed, these findings support a similar reductive elimination mechanism of PNP-supported complexes involving the intermediacy of such mixed-valent species as proposed above.

Using the dppm-supported system discussed above as a benchmark, we probed the behavior of a bimetallic system with a five-atom linker which could perturb intramolecular metal-

metal interactions. We envisioned that a longer linker (such as 1,3-(diphenylphosphino)propane (dppp)) between Au atoms might preclude formation of a 7-membered metallacyclic Au(II)-Au(II) intermediate upon oxidation. Indeed, the only product of low-temperature oxidation of dppp[Au(4-F-C$_6$H$_4$)]$_2$ (**11**) by PhICl$_2$ is mixed-valent species **13** (two 1:1 ^{19}F NMR singlets at −118.3 and −118.6 ppm and two 1:1 ^{31}P NMR singlets at 27.3 and 21.7 ppm), presumably formed via fast isomerization of **12** (Figure 6). Even at −80 °C, no signals consistent with a symmetric bimetallic Au(II) species are observed, suggestive that a mixed-valent species is formed directly upon oxidation. Upon warming to −52 °C, **13** undergoes first-order reductive elimination to dppp(AuCl)$_2$ and 4,4'-difluorobiphenyl (k. = (3.0 ± 0.1)×10^{-5} s^{-1}). Hence, the kinetic profiles of oxidation and reductive elimination of bimetallic complexes bearing linkers that restrict metal-metal interactions resemble that of mononuclear species.

Importantly, these studies reveal that access to a kinetic bimetallic Au(II) product of oxidation does not necessarily compromise the rate of reductive elimination from Au(III); in fact, the rate of reductive elimination from dppm-supported **10** is about an order of magnitude faster than that of **13**, perhaps due to increased steric crowding as a result of a shorter linker, aurophilic interactions between the Au centers in **10**, or a combination thereof. Even Au(II)/Au(II) → Au(I)/Au(III) isomerization for PNP and dppm-supported complexes is a facile process at temperatures below 0 °C.

Conclusion

We have uncovered several unexpected properties of oxidized gold that are contrary to established ideas. First, C-C bond reductive elimination from Au(III) does not necessarily require phosphine dissociation. By avoiding this rate-limiting process, biaryl reductive eliminations from Au(III) are remarkably fast, and occur as low as −52 °C. Furthermore, by judicious choice of ligand, the barrier to oxidation of bimetallic Au(I) complexes may be reduced, allowing access to symmetric intermediates with Au(II)-Au(II) bonds. When stabilized by dppm, these complexes undergo fast isomerization and reductive elimination at very low temperature; when stabilized by more rigid PNP-type ligands, they may be arrested, although at slightly higher temperatures, isomerization and reductive elimination become facile.

The stoichiometric behavior of the complexes reported in this study inform the development of catalysis involving Au(I)/Au(III) redox cycling. For instance, that phosphine dissociation is not required for C-C bond formation may slow or entirely preclude deleterious ligand oxidation by excess oxidant under conditions relevant to catalysis. Efforts to develop gold-catalyzed transformations using relatively weak oxidants compatible with substrates should focus on bimetallic Au(I) precatalysts with three-atom linkers, such as PNP or dppm. Given that transmetalation to Au(I) can be achieved at temperatures as low as −78 °C[50], and that Au(I) oxidation, isomerization and reductive elimination are facile processes below 0 °C, catalysis may be achieved at temperatures low enough to avoid unwanted side reactions between oxidant and substrate. Investigations probing ligand and electronic effects on the reductive elimination at Au(III), and stoichiometric reactivity of bimetallic Au(II)

complexes are ongoing to further our nascent understanding of the fundamental chemistry of oxidized gold.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENT

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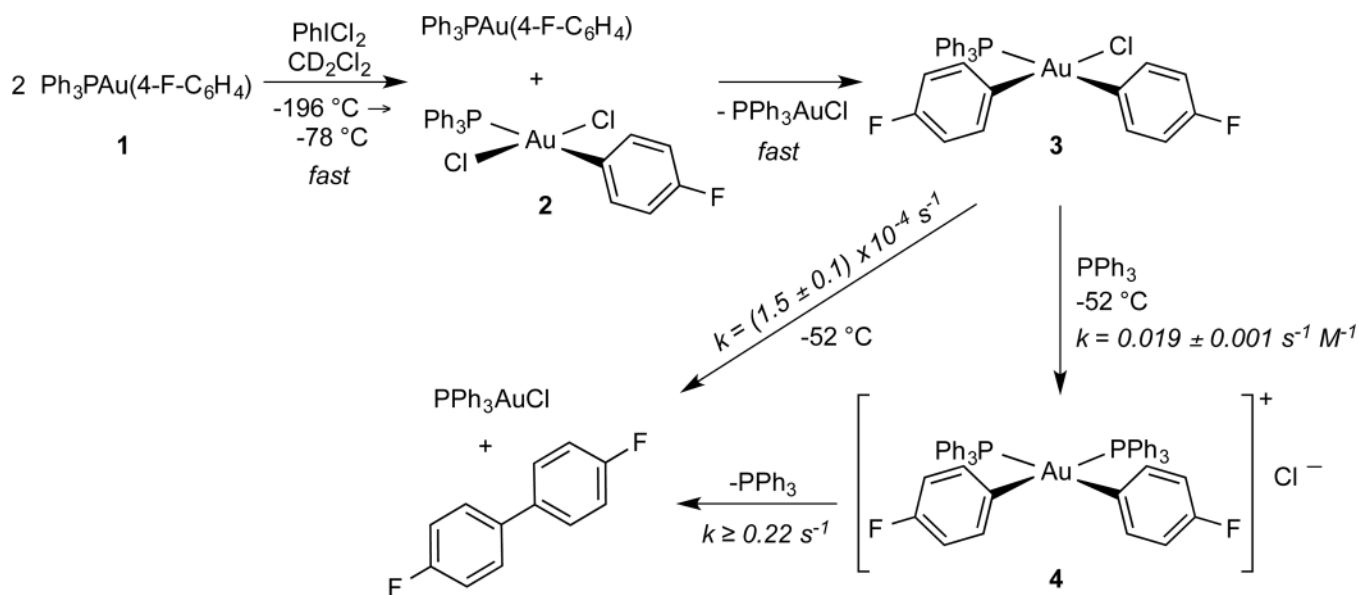
Figure 1.
Oxidation of monometallic Au(I) and biaryl reductive elimination from Au(III). A CD_2Cl_2 solution of $Ph_3PAu(4\text{-}F\text{-}C_6H_4)$ (**1**) undergoes fast partial oxidation by $PhICl_2$ upon thawing at low temperature to afford **2**, which reacts rapidly with remaining **1** to generate a *cis*-diaryl Au(III) species (**3**). Reductive elimination from **3** affords 4,4'-difluorobiphenyl. Associative ligand exchange of **3** with excess PPh_3 generates cationic **4**, which undergoes very fast biaryl reductive elimination.
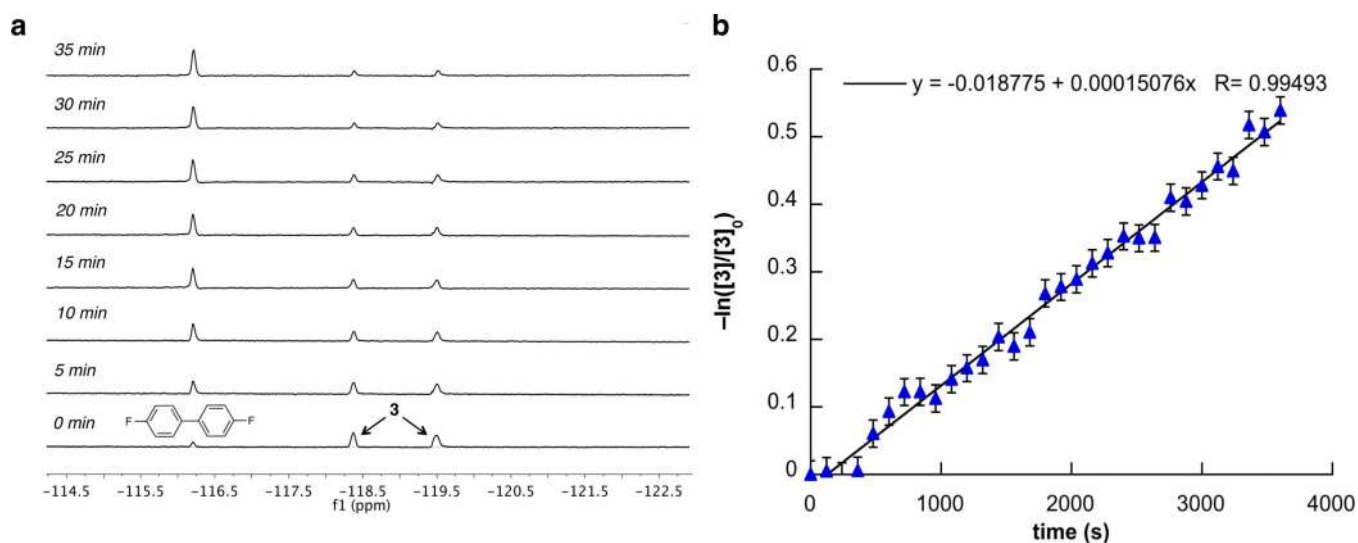
Figure 2.
Kinetics of decay of *cis*-(Ph$_3$P)Au(4-F-C$_6$H$_4$)$_2$Cl (**3**). **a**, First-order decay of **3** monitored by ^{19}F NMR (470 MHz, CD$_2$Cl$_2$) at −32 °C over a period of 35 minutes. **b**, A natural log plot of [**3**]/[**3**]$_{t=0}$ indicative of a first order process. Error bars represent the inherent error in quantifying ^{19}F NMR signal intensity.

Figure 3.
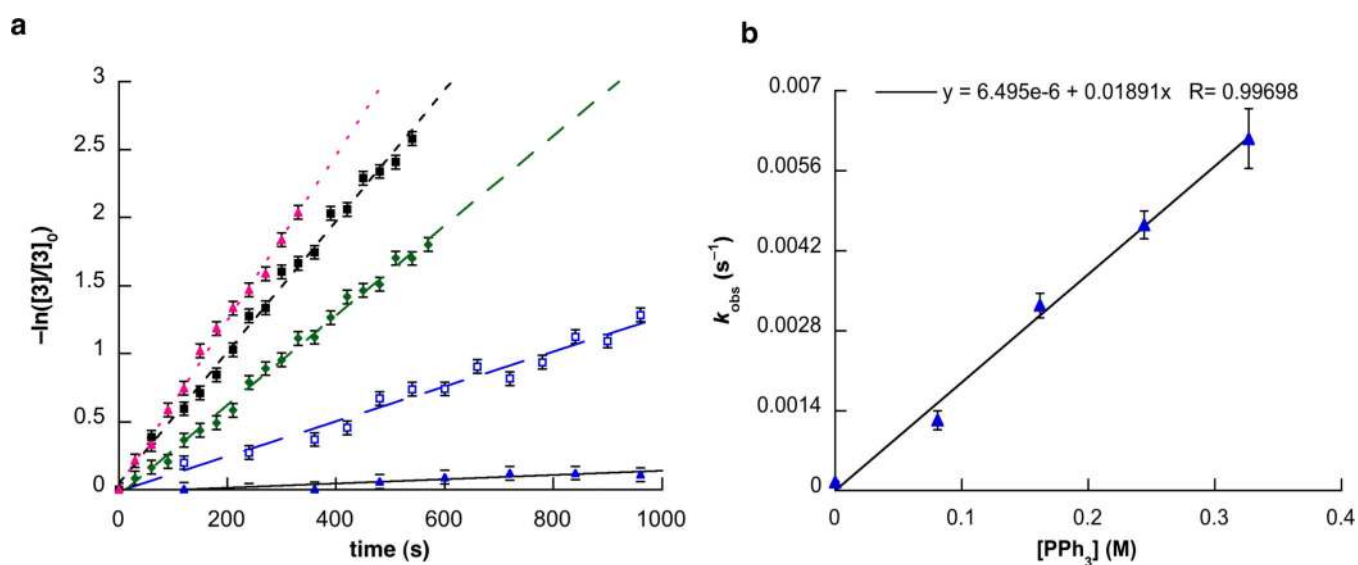Unexpected phosphine acceleration on the decay of **3** at −52 °C. **a,**,The rate of decay of **3** (slope of the natural log plot) increases with [PPh$_3$] (▲ (0 equiv PPh$_3$); □ (10 equiv PPh$_3$); ◆ (20 equiv PPh$_3$); ■ (30 equiv PPh$_3$); ▲ (40 equiv PPh$_3$)). **b**, A linear relationship between [PPh$_3$] and k_{obs} for the decay of **3** in the presence of excess PPh$_3$ (pseudo-first order conditions), indicating that ligand exchange from **3** to **4** is first-order in PPh$_3$. Error bars represent the inherent error in interpreting ^{19}F NMR signal intensity (**a**) or the standard deviation over three separate experiments (**b**).
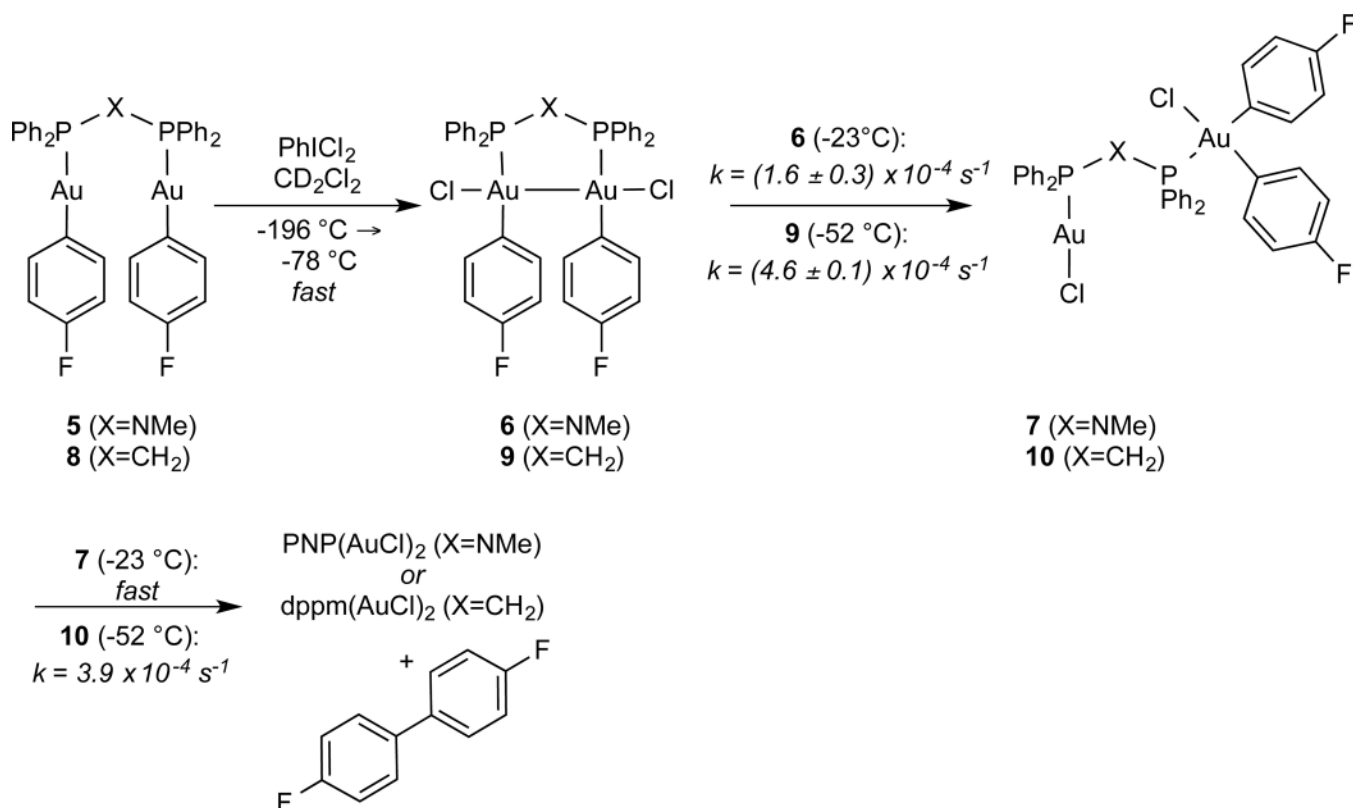
Figure 4.
Oxidation of bimetallic Au(I)/Au(I) complexes is under kinetic control, affording Au(II)/Au(II) intermediates which isomerize to mixed-valent Au(I)/Au(III) species and reductively eliminate biaryl from a single metal center. Solutions of PNP[Au(4-F-C_6H_4)]$_2$ (**5**) and dppm[Au(4-F-C_6H_4)]$_2$ (**8**) undergo fast oxidation by PhICl$_2$ upon thawing to generate intermediates stabilized by intramolecular Au(II)-Au(II) bonds. Complex **6** undergoes isomerization slower than **9**, perhaps due to decreased ligand flexibility. Since isomerization for PNP-supported complexes is rate-limiting, reductive elimination from **7** is unobservable. In contrast, the rates of isomerization and reductive elimination of dppm-supported complexes are comparable, allowing kinetic analysis of both steps to preclude the possibility of a bimetallic reductive elimination directly from **9**.
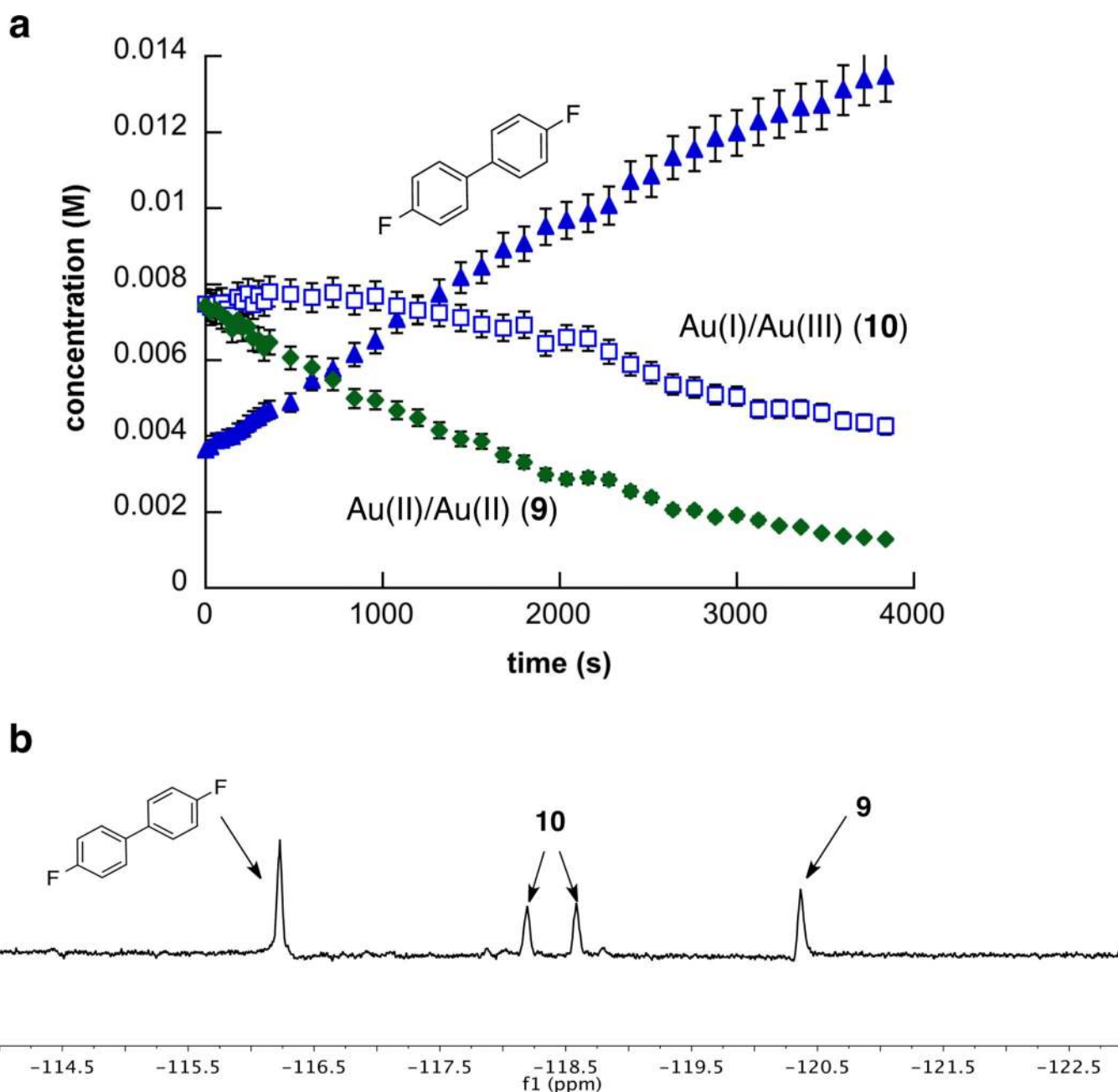
Figure 5.
Monitoring oxidation of dppm[Au(4-F-C$_6$H$_4$)]$_2$ (**8**) to Au(II)/Au(II) intermediate **8**, isomerization to Au(I)/Au(III) species **10** and reductive elimination of 4,4'-difluorobiphenyl. **a**, Reaction profile for the isomerization of **9** to **10** and reductive elimination of biaryl from **10** at −52 °C, monitored by ^{19}F NMR. **b**, Selected region of ^{19}F NMR spectrum (470 MHz, CD$_2$Cl$_2$) of oxidation of **8** at −52 °C. Complex **8** has been fully consumed. The equivalent fluorides of Au(II)/Au(II) species **9** are clearly visible at −120.3 ppm, as are the inequivalent fluorides in Au(I)/Au(III) species **10** at −118.2 and −118.6 ppm. Error bars represent the inherent error in interpreting ^{19}F NMR signal intensity.
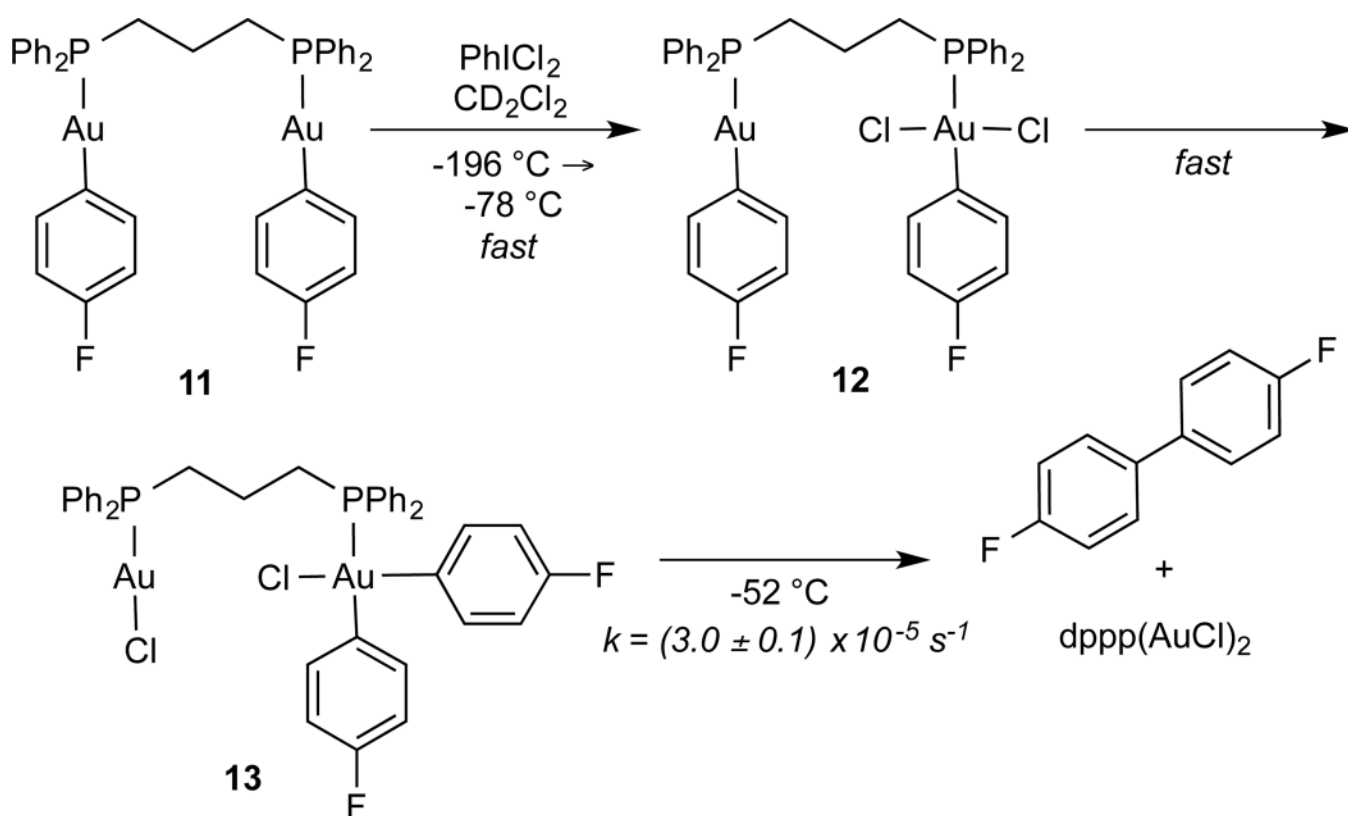
Figure 6.
Five-atom linker dppp discourages formation of Au(II)/Au(II) intermediates upon oxidation of bimetallic dppp[Au(4-F-C$_6$H$_4$)]$_2$ (**11**). Solutions of **11** undergo fast oxidation by PhICl$_2$ upon thawing to afford directly the unobservable Au(I)/Au(III) complex **12**, which isomerizes to **13.** Reductive elimination from **13** affords 4,4'-difluorobiphenyl.